

# An ORGANIC LOW K DIELECTRIC ETCH WITH NH<sub>3</sub> CHEMISTRY

## Background of Invention

### 1) Field of the Invention

This invention relates generally to fabrication of semiconductor devices and more particularly to the etching of organic low -k dielectric layers and particularly an etch process for organic low K layers that uses a ammonia based chemistry (e.g., pure ammonia or ammonia with (H<sub>2</sub> or N<sub>2</sub>)).

### 2) Description of the Prior Art

Traditional etch chemistry for the organic low-k material is N<sub>2</sub> related chemistry, such as N<sub>2</sub>/O<sub>2</sub> and H<sub>2</sub>/H<sub>2</sub> etc. The excellent physical profile of the damascene structure can be obtained by N<sub>2</sub>/H<sub>2</sub> chemistry with a lower etch rate, compared to N<sub>2</sub>/O<sub>2</sub> chemistry. However, it is very likely to get a bowing sidewall profiles (e.g., non-vertical sidewalls) by N<sub>2</sub>/O<sub>2</sub> chemistry.

The importance of overcoming the various deficiencies noted above is evidenced by the extensive technological development directed to the subject, as documented by the relevant patent and technical literature. The closest and apparently more relevant technical developments in the patent literature can be gleaned by considering US 6,071,815 (Kleinhenz et al.) that shows a silicon oxide layer etch that uses HF and ammonia in combination with other gases.

US 5,897,377 (Suzuki) shows a surface treatment etch.

US 5,972,235 (Brigham et al.) shows a low-k etch.

1                   US 6,063,712 (Gilton et al.) teaches an oxide etch  
2   using ammonia a fluorine containing compound and a boron  
3   containing compound.

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6                   However, further improvement is needed to etch  
7   organic low-K materials.

## Summary of the Invention

It is an object of the present invention to provide a method for etching low -k dielectric layers.

It is an object of the present invention to provide a method for etching low -k dielectric layers that uses an ammonia based chemistry.

It is an object of the present invention to provide a method for etching low -k dielectric layers that uses an pure ammonia or  $\text{NH}_3$  /  $\text{H}_2$  or  $\text{NH}_3$  /  $\text{N}_2$  etch gasses plus optionally CO and/or  $\text{O}_2$  .

To accomplish the above objectives, the present invention provides a method which is characterized as follows. An organic low k dielectric layer is formed over a substrate. A resist pattern is formed over the low k dielectric layer. The resist pattern has an opening.

Using the invention's etch process, the organic low k dielectric layer is etched through the opening in an etch mask. The invention's etch process comprise a  $\text{NH}_3$  containing plasma etch (optionally with  $\text{H}_2$  or  $\text{N}_2$ ).

The invention's  $\text{NH}_3$  containing plasma etch etches Low- k materials unexpectedly well. The invention's  $\text{NH}_3$  only etch had a 30 to 80% higher etch rate than conventional  $\text{N}_2/\text{H}_2$  etches of low-k materials like Silk <sup>TM</sup>.

Additional objects and advantages of the invention will be set forth in the description that follows, and in part will be obvious from the description, or may be learned by practice of the invention. The objects and advantages of the invention may be realized and obtained by means of

- 1 instrumentalities and combinations particularly pointed out in
- 2 the append claims.

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### Brief Description of the Drawings

The features and advantages of a semiconductor device according to the present invention and further details of a process of fabricating such a semiconductor device in accordance with the present invention will be more clearly understood from the following description taken in conjunction with the accompanying drawings in which like reference numerals designate similar or corresponding elements, regions and portions and in which:

Figures 1 and 2 are cross sectional views for illustrating an etch process for etching organic low k materials in a single damascene structure according to the present invention.

Figures 3 and 5 are cross sectional views for illustrating an etch process for etching organic low k materials in a dual damascene structure according to the present invention.

FIG 6A shows the chemical structure for PAE.

FIG 6B shows the chemical structure for Silk<sup>TM</sup> (A PAE containing organic dielectric with aromatic rings).

## Detailed Description of the Preferred Embodiments

### I. Overview - $\text{NH}_3$ based etch for organic low K dielectric layers

To accomplish the above objectives, the present invention provides a method for etching organic low-k dielectric layers which is characterized as follows.

#### organic low K compositions

The invention is an ammonia etch ( $\text{NH}_3$ ) chemistry for organic low K layers. "Low K" means dielectric constants less than or equal to 3.0. The organic low k dielectric layers can be any organic dielectric material with a dielectric constant less than or equal to 3.0. These dielectric layers are made from organic containing reactants. Examples of two types of low k materials are: 1) organic /Spin on (e.g., K = ~ 2.6 to 2.7 (Silk<sup>TM</sup> and Flare<sup>TM</sup> by made by Allied signal (e.g., fluorinated arylether)) and 2) oxide/CVD (k= 2.7 to 3.0) (e.g., Black diamond<sup>TM</sup>, coral<sup>TM</sup> etc. e.g., carbon doped oxides)

Other organic low k materials are PAE II, Benzocyclobuthene (BCB), amorphous teflon (Polytetrafluoroethylene) and Parylene. Also, HOSP<sup>TM</sup> from AlliedSignal, hydrogen silsequioxane (HSQ) for example FOX<sup>tm</sup> flowable oxide brand HSQ.

One such organic low k dielectric layer is comprised of poly arylene ether (PAE) possibly with other functional groups - See FIG 6A for the chemical structure of PAE.

FIG 6B shows the chemical structure of SiLK™ (e.g., Silk™ made by Dow chemical ). Another example of a low-k dielectric. Silk™ has aromatic groups which can be etched with O<sub>2</sub> based H<sub>2</sub> /H<sub>2</sub> and NH<sub>3</sub> based chemistries. It is possible that N<sub>x</sub>H<sub>y</sub> and H radicals attack the rings during the etch.

The invention's NH<sub>3</sub> containing etch is preferably used to PAE containing low K materials such as SilK™ and Flare™.

#### **A. Etch process - 1<sup>st</sup> embodiment - NH<sub>3</sub> only**

In a first embodiment of the invention's NH<sub>3</sub> containing etch, the etch process comprises: etching the low k dielectric layer 20 by applying a plasma power and flowing only NH<sub>3</sub> gas. It is critical that only NH<sub>3</sub> gas is flowed. It is not proper to use another N and/or H containing gas such as N<sub>2</sub>/H<sub>2</sub>.

The 1<sup>st</sup> embodiment uses NH<sub>3</sub> only with a power in between 500 and 1500 W, medium plasma power plasma density between 1E9 and 1E11 cm<sup>-3</sup> and a NH<sub>3</sub> flow between 50 and 300 sccm and a pressure between 80 and 800 mTorr. Typical process is power 1000 W and a NH<sub>3</sub> flow 200 sccm and a pressure 100 mTorr (all values range +/- 5).

Also the 1<sup>st</sup> embodiment forms a substantially vertical sidewall (between 87 and 93 degrees to the surface of the substrate.

**B. second embodiment  $\text{NH}_3$  and  $\text{H}_2$** 

In a second embodiment, etch process comprises: etching the low k dielectric layer (e.g. 20, FIG 1) by applying a medium plasma density between  $1\text{E}9$  and  $1\text{E}11\text{ cm}^{-3}$  and flowing  $\text{NH}_3$  gas and  $\text{H}_2$  gas.

The 2<sup>ND</sup> embodiment uses  $\text{NH}_3$  and  $\text{H}_2$  with a plasma power between 500 and 1500 W, medium plasma power plasma density between  $1\text{E}9$  and  $1\text{E}11\text{ cm}^{-3}$ , a  $\text{NH}_3$  flow between 50 and 300 sccm, a  $\text{H}_2$  flow between 50 and 300 sccm and a pressure between 80 and 800 mTorr. Typical process parameters are power 1000 W and a  $\text{NH}_3$  flow 100 sccm,  $\text{H}_2$  flow about 200 sccm and a pressure 100 mTorr (all values range +/- 5).

**C. 3<sup>rd</sup> embodiment -  $\text{NH}_3$  and  $\text{N}_2$** 

The 3<sup>ND</sup> embodiment uses  $\text{NH}_3$  and  $\text{N}_2$  with a power in between 500 and 1500 W, medium plasma power plasma density between  $1\text{E}9$  and  $1\text{E}11\text{ cm}^{-3}$ , a  $\text{NH}_3$  flow between 50 and 300 sccm and a  $\text{N}_2$  flow between 50 and 300 sccm and a pressure between 80 and 800 mTorr. Typical process is power 1000 W and a  $\text{NH}_3$  flow 67 sccm,  $\text{N}_2$  flow about 266 sccm, and a pressure 100 mTorr (all values range +/- 5).

**D. Optional  $\text{CO}$  and  $\text{O}_2$** 

All embodiments of the invention's  $\text{NH}_3$  containing etch can include additional  $\text{CO}$  and  $\text{O}_2$  flows. The  $\text{CO}$  and  $\text{O}_2$  are thought to remove polymer from the low K layer sidewalls and can create bowed (non vertical) sidewall profiles.



### **E. Medium density process and Tool**

It is important to realize that the processes (all embodiments) are preferably performed in a medium plasma density between  $1\text{E}9$  and  $1\text{E}11\text{ cm}^{-3}$ . This is contrast with High density plasma between  $1.1\text{E}11$  and  $1\text{E}12\text{ cm}^{-3}$ . The invention can be performed in a medium density tool, TEL's Rie tools models DRM and SCCM. Thus the process in DRM should also work for SCCM in a similar way.

The invention's medium density tools contrast with High density plasma tools (plasma density between  $1\text{E}11$  and  $1\text{E}12\text{ cm}^{-3}$ ) such as Applied Materials IPS and LAM's TCP 9100.

## **II. Invention's hard mask etch step**

Below are example process for single and dual damascene structure. Any of the hard mask (HM) layers or stop layers (e.g., via and trench liner stop layers) can be etched by the following process.

The hard mask (HM) or stop layer etch step preferably comprises: a  $\text{CF}_4$  / $\text{O}_2$  /Ar or  $\text{C}_4\text{F}_8$  / $\text{O}_2$  /Ar etch flow with a power between 1000 and 1500 W, a pressure between 40 and 50 mTorr and a  $\text{CF}_4$  flow between 40 and 80 sccm ( $\text{C}_4\text{H}_8$  between 8 and 12 sccm),  $\text{O}_2$  flow between 5 and 20 sccm and Ar flow between 100 and 200 sccm, and medium plasma density between  $1\text{E}9$  and  $1\text{E}11\text{ cm}^{-3}$ .

### 1    **III. Single Damascene structure**

2                    FIGS 1 and 2 show an option for a single damascene  
3 structure.

4                    A semiconductor structure 10 14 is provided.  
5 Semiconductor Structure 10 is understood to possibly include a  
6 semiconductor wafer 10, active and passive devices formed within  
7 the wafer; and insulating and conductive layers (e.g., 14)  
8 formed on the wafer surface. For example, layer 14 can be an  
9 insulating layer such as an inter metal dielectric (IMD) layer  
10 or an etch stop layer.

11                   Over the substrate 10 the following layers are  
12 preferably formed. A stop liner layer 20 preferably with a  
13 thickness of between about 300 and 500 Å. Next, we form a first  
14 low k organic inter metal dielectric (IMD) layer 24 preferably  
15 with a thickness between 2000 and 4000 Å. Over that, we form a  
16 hardmask layer 30 with a thickness between 500 and 2500 Å. The  
17 stop liner and hard mask layers can be made of silicon oxide,  
18 Silicon oxynitride(SiON), carbide or Silicon nitride (SiN) and  
19 are preferably formed of SiN. Next, we form a resist layer 40  
20 with a first opening 44.

21                   The wafer is placed in an etch tool. The following  
22 etch steps are preferably performed insitu.

#### 23                   **A.    HM open etch step**

24                   A hard mask (HM) open etch step is performed to etch  
25 thru the HM layer 30. The HM etch step preferably comprises: a  
26  $\text{CF}_4$  / $\text{O}_2$  /Ar or  $\text{C}_4\text{F}_8$ / $\text{O}_2$  /Ar etch with a power between 1000 and 1500  
27 W, a pressure between 40 and 50 mTorr and a  $\text{CF}_4$  flow between 40  
28 and 80 sccm ( $\text{C}_4\text{F}_8$  between 8 and 12 sccm),  $\text{O}_2$  flow between 5 and  
29 20 sccm and Ar flow between 100 and 200 sccm.

## **B. organic Low K dielectric etch step**

Next, we etch thru organic Low K dielectric layer 24 using one of invention's embodiments for the  $\text{NH}_3$  based etch. (See above). During the etch, the photoresist can be removed (e.g., demonstrated  $\text{NH}_3$  based resist ashing).

## **C. Stop liner etch**

Next, a stop liner etch step is performed preferably using the following parameters: a  $\text{CH}_x\text{F}_y/\text{O}_2/\text{Ar}$  (such as  $\text{CH}_2\text{F}_2/\text{O}_2/\text{Ar}$  or  $\text{CHF}_3/\text{O}_2/\text{Ar}$  flow) with a RF power between 300 and 500 W, pressure between 30 and 40 mtorr,  $\text{CH}_2\text{F}_2$  flow between 10 and 20 sccm ( $\text{CHF}_3$  between 10 and 20 sccm),  $\text{O}_2$  flow between 5 and 20 sccm, and Ar flow between 100 and 200 sccm.

FIG 2 shows the structure after the etch steps and opening 50 is formed.

## **IV. dual Damascene process**

FIGS 3, 4 and 5 show a preferred process for a dual damascene process.

FIG 3 shows the following structure:

Substrate 10 (e.g., SI wafer)  
 dielectric layer 114 (e.g., inter metal dielectric)  
 via stop layer - thickness between 300 and 500 Å  
 first organic IMD layer 128 - thickness between 3000 and 5000 Å  
 trench stop layer 134 - (optional) thickness between 0 and 500 Å  
 organic IMD trench layer (second IMD layer)- thickness between 3000 and 5000 Å.  
 second hard mask 144 - 500 and 1500 Å  
 first hard mask 148 - 1500 and 2500 Å

1           The hard mask (HM) 144 148 and stop layers 122 134  
2   can be formed of silicon oxide, SiON, carbide or SIN and are  
3   preferably formed of silicon nitride (SiN).

4           **A.    HM1 open for via**

5           As shown in FIG 3, in a first etch step, the HM1 148  
6   is etched to form a first HM opening. The hard mask open etch  
7   is the same as describe above in the single damascene process.

8           **B.    Via etch in trench layer with resist removal**

9           The next etch step is a via etch of the second  
10   organic low - k inter metal dielectric layer 138 to form first  
11   opening 154 (See FIG 3). During the etch, the photoresist can  
12   be removed (e.g., demonstrated NH<sub>3</sub> based resist ashing). .

13           Any of the invention's NH<sub>3</sub> based etch embodiments  
14   can be used.

15           **C.    Trench stop layer 134 & HM 2 144 etch**

16           As shown in FIG 4, a trench stop layer 134 & HM2 144  
17   etch step is performed to form HM opening 155 and to remove the  
18   trench stop layer 134 in opening 154. This step can the same  
19   etch as the HM open etch steps. See above.

20           **D.    Trench and via etch**

21           As shown in FIG 5, the trench opening 164 and via  
22   opening 160 are formed by an etch using the HM1 148 and trench  
23   stop 134 as etch masks. The etch etches the organic low k layers  
24   138 and 128 to form trench opening 164 and via opening 160. The  
25   etch uses the invention's NH<sub>3</sub> containing etch.

### **E. trench liner 134 and via stop liner 122 etch**

Still referring to FIG 5, the trench liner 134 and via stop liner 122 are etched to remove the trench liner 134 and via stop liner 122 in the openings 164 and 160. The trench liner etch is the same as describe above in the single damascene process (E.g.,  $\text{CH}_2\text{F}_4/\text{O}_2$  /AR or  $\text{CHF}_4/\text{O}_2$  /Ar etch).

### **F. Benefits of the invention**

The invention's  $\text{NH}_3$  containing plasma etch etches organic Low- k materials unexpectedly well and fast. This increases the etch rate without forming polymers and allows for vertical sidewalls of the low- k material.

The invention's  $\text{NH}_3$  only etch had a 30 to 80% high etch rate than conventional  $\text{N}_2/\text{H}_2$  etches of low-k materials like Silk TM (e.g., PAE containing dielectric layers).

## **V. Examples**

The inventors performed the following experiments.

### **Etch rate comparison**

Gas flow ratio	Etch rate (K Å/min)
100 $\text{N}_2$ /300 $\text{H}_2$	1.6
200 $\text{NH}_3$	3
50 $\text{N}_2$ /350 $\text{H}_2$	1.4
100 $\text{NH}_3$ /200 $\text{H}_2$	2.4
100 $\text{NH}_3$ /200 $\text{H}_2$	1.7
67 $\text{NH}_3$ /366 $\text{H}_2$	2.6

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2 With same atomic ratio, the invention's  $\text{NH}_3$  based  
3 chemistry produced a higher etch rate.

4 Unless explicitly stated otherwise, each numerical  
5 value and range should be interpreted as being approximate as if  
6 the word about or approximately preceded the value of the  
7 value or range.

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9  
10 In the above description numerous specific details  
11 are set forth such as flow rates, pressure settings,  
12 thicknesses, etc., in order to provide a more thorough  
13 understanding of the present invention. It will be obvious,  
14 however, to one skilled in the art that the present invention  
15 may be practiced without these details. In other instances,  
16 well known process have not been described in detail in order to  
17 not unnecessarily obscure the present invention. Also, the flow  
18 rates in the specification can be scaled up or down keeping the  
19 same molar % or ratios to accommodate difference sized reactors  
20 as is known to those skilled in the art.

21 Although this invention has been described relative  
22 to specific insulating materials, conductive materials and  
23 apparatuses for depositing and etching these materials, it is  
24 not limited to the specific materials or apparatuses but only to  
25 their specific characteristics, such as conformal and non-  
26 conformal, and capabilities, such as depositing and etching, and  
27 other materials and apparatus can be substituted as is well  
28 understood by those skilled in the microelectronics arts after  
29 appreciating the present invention

1           Within the present invention, the substrate may be a  
2 substrate employed within a microelectronics fabrication  
3 selected from the group including but not limited to integrated  
4 circuit microelectronics fabrications, solar cell  
5 microelectronics fabrications, ceramic substrate  
6 microelectronics fabrications and flat panel display  
7 microelectronics fabrications. Although not specifically  
8 illustrated within the schematic cross-sectional diagram of Fig.  
9 1, the substrate 10 may be the substrate itself employed within  
10 the microelectronics fabrication, or in the alternative, the  
11 substrate may be the substrate employed within tile  
12 microelectronics fabrication, where the substrate has formed  
13 thereupon or thereover any of several additional  
14 microelectronics layers as are conventionally employed within  
15 the microelectronics fabrication, Such additional  
16 microelectronics layers may include, but are not limited to,  
17 microelectronics conductor layers, microelectronics  
18 semiconductor layers and microelectronics dielectric layers.

19  
20           While the invention has been particularly shown and  
21 described with reference to the preferred embodiments thereof,  
22 it will be understood by those skilled in the art that various  
23 changes in form and details may be made without departing from  
24 the spirit and scope of the invention. It is intended to cover  
25 various modifications and similar arrangements and procedures,  
26 and the scope of the appended claims therefore should be  
27 accorded the broadest interpretation so as to encompass all such  
28 modifications and similar arrangements and procedures.

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2 What is claimed is:

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